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平成１６年登簿第　　／／／　号

認　　証

嘱託人三宅有紀は、本公証人の面前で、別添文書に署名した。

よって、これを認証する。

平成１６年　５月　１２日、本公証人役場において

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証　　明

上記署名は、東京法務局所属公証人の署名に相違ないものであり、かつ、その押印は、真実のものであることを証明する。

平成１６年　５月１２日

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APOSTILLE

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MINISTRY OF FOREIGN AFFAIRS · JAPAN ·

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DECLARATION

I, Yuki MIYAKE residing at 1223-1 A-409, Sonno-cho, Inage-ku, Chiba-shi, Chiba, 263-0051, Japan do hereby solemnly and sincerely declare:

1. That I am an employee of Furuya & Co. located at Hamacho-Hanacho Building, 2-17-8, Nihonbashi-Hamacho, Chuo-ku, Tokyo 103-0007,Japan,
2. That I am well acquainted with the Japanese and English languages, and
3. That the attached English document is a true and correct translation into English of the certified copy of the Japanese patent application No. 6-320108 filed on 22 December 1994, a copy of which is hereto attached.

三宅有紀

And I make this solemn declaration conscientiously believing the same to be true and correct.

on the date of 12 May 2004

三宅有紀

By Yuki MIYAKE

This is to certify that this document was subscribed before me by the above-named person(s) on this day.

MAY 12 2004

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Patent Office
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This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: 22 December 1994

Application Number: patent application No. 6-320108

Applicant(s): Daicel Chemical Industries, Ltd.

dated 5 January 1996

Commissioner

Patent Office

Mr. Yuji KIYOKAWA

Shusho No.
Shushotokuhei 07-3078267

[Designation of Document] Patent Application

[Reference Number] 194DK108

[Application Date] 22 December 1994

[Addressee] the Commissioner of the Patent Office

[IPC] C06D 5/06

[Title of the Invention] Gas Generant Composition

[Number of Claims] 6

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【Designation of Document】 Specification

【Title of the Invention】 Gas Generant Composition

【Claims】

【Claim 1】 A gas generant composition having, as the essential components, a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer, which comprises a mixture of manganese dioxide and one or at least two metal oxides selected from the group consisting of copper oxides, cobalt oxides, iron oxides and silver oxides.

【Claim 2】 The gas generant composition according to claim 1, wherein the metal oxide is one or at least two selected from the group consisting of CuO, Cu_2O, Co_3O_4, Fe_2O_3 and Ag_2O.

【Claim 3】 The gas generant composition according to claim 1 or 2, wherein the nitrogen-containing organic compound is at least one selected from the group consisting of organic compounds containing amino group or amido group and tetrazole derivatives.

【Claim 4】 The gas generant composition according to claim 3, wherein the organic compound containing amino group or amido group is azodicarbonamide.

【Claim 5】 The gas generant composition according to claim 3, wherein the tetrazole derivative is aminotetrazole.

【Claim 6】 The gas generant composition according to any one of

claims 1 to 5, wherein the oxygen-containing inorganic oxidizer is at least one selected from the group consisting of KNO_3, $Sr(NO_3)_2$ and $KClO_4$.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a gas generant composition. More specifically, the invention relates to a non-azide type gas generator composition which supplies gas components by burning for the purpose of inflating an air bag in an air bag system.

[0002]

[Prior Art]

In the event of collision of vehicles like cars at high speed, the driver and passengers might be injured or killed by clashing against internal hard or dangerous parts of the vehicles such as the handle and front glass. In order to prevent such disasters, air bag systems for automobiles have been developed which inflate quickly by a gas generated from a gas generant.

Requirements for the gas generant of an automobile air bag system are very severe. At first, the bag should inflate in a very short period of time, usually not longer than 40 to 50 milliseconds. Further, The atmosphere within the bag is most suitable when it corresponds to the air composition in the car. These requirements

are satisfied by gas generants which have been currently used in common comprising a base gas generant such as alkali metal salts (in particular sodium azide) or alkaline earth metal salts of hydrazoic acid. However, these gas generants are seriously defective in that the main component, sodium azide is toxic and that the by-products alkali components are also toxic. Hence, environmental pollution brought by a large amount of scrap cars and health hazard of the driver and passengers when the gas is generated are concerned.

[0003]

For the purpose of overcoming these problems, non-azide type gas generants have been under development in place of sodium azide type. For example, JP-A 3-208878 discloses a composition which comprises a main component of oxygen-containing oxidizer such as tetrazole, triazole, or their metal salts combined with ammonium perchlorate or sodium nitrate and an auxiliary component of a metal oxide such as V_2O_5, CuO or Fe_2O_3. The metal oxide mentioned forms a solid combustion product, which is easily removed by filtration when undesired components are removed by filtration prior to release the formed gas into the bag in an air bag system, and converts CO which is toxic to human bodies generated from the nitrogen-containing organic compound to CO_2. JP-B 64-6156 and JP-B 64-6157 disclose a gas generant which contains, as the main component, a metal salt of bitetrazole compound that does not contain hydrogen. JP-A 3-208878 further discloses a gas generant having a transition metal complex

of aminoarazole as the main component. These non-azide type compounds disclosed in the series of prior art references are characteristic in that the concentration of carbon monoxide released is low since the carbon number in the one molecule is small; however, the amount of nitrogen oxides, toxic to human bodies, increases in all the cases and the performance is not satisfactory in respect of the inflation period of the bag.

[0004]

[Problems to be Solved by the Invention]

The present inventors previously had found that a non-azide type gas generant having a nitrogen-containing organic compound such as azodicarbonamide and a certain inorganic oxygen-containing oxidizer as the effective component is free from environmental pollution, satisfactory in respect of the inflation period of the bag, and advantageous in the cost, and filed the patent applications (with reference of JP-A 4-185251, JP-A 4-185253 and JP-A 5-18782).

[0005]

In the combustion of an organic compound containing nitrogen, it is well-known that carbon monoxide will generate as incomplete combustion product even when an oxidizer is used in an amount exceeding the chemical equivalence that releases the necessary amount of oxygen for burning combustible elements, such as carbon, hydrogen and others, in the organic compound. In view of this fact, the nitrogen compound,

such as azodicarbonamide, used as the main agent in the mentioned gas generant is supposed to release a relatively rather large amount of carbon monoxide and nitrogen oxides since many carbon atoms are contained per molecule. For the purpose of avoiding such by-product carbon monoxide, it is suggested that carbon monoxide should be converted to carbon dioxide by increase of a partial pressure of oxygen in reaction caused by a largely increased amount of an oxidizing agent in the gas generant composition. However, when a gas generant burns, the highest temperature in the inflator exceeds 2,000°C and the oxygen molecules, which exists more the stoichiometric amount ratio due to increase of the partial pressure of oxygen in reaction, react with the nitrogen molecules released, whereby a large amount of nitrogen oxides called "thermal NOx" is generated. Toxicity of the NOx contained in a large amount in the released gas is said to be a main reason why non-azide type gas generants are not used in practice notwithstanding many studies. It is desirable to convert NOx to N_2 by some means for reducing the NOx. Many references including patents and papers for NOx reduction suggest that a catalyst might reduce NOx, which comes from a fixed source of automobile exhaust gas, to a certain level in the presence of a reductant. However, there are rarely known catalysts that are reactive enough in a contact period of time of several dozens milliseconds, as required for a gas generant for air bag system, without addition of a reductant.

[0006]

[Means to Solve the Problem]

As a result of intensive studies of the present inventors, it has been surprisingly found that a combination of manganese dioxide and a certain oxide has an important function for decreasing nitrogen oxides; this finding has lead to completion of the present invention.

According to the present invention, a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components is provided, which composition is characterized by containing mixed catalysts of one or more metal oxides selected from the group consisting of copper oxides, cobalt oxides, iron oxides and silver oxides.

[0007]

The gas generant composition of the present invention contains a nitrogen-containing organic compound and a oxygen-containing inorganic oxidizer as the essential components.

There is no particular limitation for the nitrogen-containing organic compound usable for the present invention provided that nitrogen atom is contained in the molecule; examples of the nitrogen-containing organic compound include organic compounds containing amino group or amido group and tetrazole derivatives. Specific examples of the organic compounds containing amino group or amido group include: azodicarbonamide, urea, aminoguanidine bicarbonate, biuret, dicyandiamide, and hydrazides; preferably azodicarbonamide. Specific examples of the tetrazole derivatives

include: aminotetrazole, tetrazole, azotetrazole, bitetrazole, tetrazole carboxylate, their alkali metal salts and their alkaline earth metal salts; and preferably aminotetrazole. The nitrogen-containing organic compound may be used in single or as a mixture of two or more kinds.

【0008】

The oxygen-containing inorganic oxidizer usable in the present invention may be selected widely from known ones such as nitrates, nitrites, and oxyhalogenates. Specific examples of the oxygen-containing inorganic oxidizer include potassium nitrate, sodium nitrate, strontium nitrate, potassium nitrite, sodium nitrite, sodium perchlorate, potassium perchlorate, sodium chlorate, and potassium chlorate. More specifically, a single compound or mixture selected from KNO_3, $Sr(NO_3)_2$ and $KClO_4$ may be used; $KClO_4$ is preferable in particular.

【0009】

The blend ratio of the nitrogen-containing organic compound to oxygen-containing inorganic oxidizer in the gas generant composition of the present invention may be optionally selected depending on the combustion rate, combustion temperature and combustion temperature, although the ratio is normally selected so as to be stoichiometric when the nitrogen-containing organic compound is completely oxidized and burned on the basis of the oxygen amount. For example, about 20 through 400 parts by weight of the oxygen-containing inorganic

oxidizer is blended with 100 parts by weight of the nitrogen-containing organic compound; blending some excess amount of the oxygen-containing inorganic oxidizer compared to the stoichiometric amount for complete combustion is preferred for enhancing the efficiency of oxidizer catalyst provided that the gas generation efficiency based on the unit weight of the gas generant composition is not substantially lowered.

【0010】

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, mixed catalysts of manganese dioxide and at least one metal oxide selected from the group consisting of copper oxides, cobalt oxides, iron oxides and silver oxides is further blended. The manganese dioxide can be prepared according to a well-known method in this field. For example, it can be prepared by the method described in Page 411 to 412 in "Genso Betsu Shokubai Binran (Handbook on Catalysts by Elements) (edited by Catalysis Society of Japan, issued by Chijinshokan Co., Ltd.), by the method disclosed in DE-B 1593320, or by the method disclosed in JP-A 3-68447, however, any other method than the above can be employed. Additionally, a method of preparing the metal oxides used in the present invention is not particularly limited, either. Among the metal oxides mentioned above, at least one selected from the group consisting of CuO, Cu_2O, Co_3O_4, Fe_2O_3 and Ag_2O is effective in the present

invention.

In mixed catalysts in the invention, comprising manganese dioxide and the one or more metal oxides selected from the group consisting of copper oxides, cobalt oxides, iron oxides and silver oxides, a blending ratio of the manganese dioxide to the metal oxides is preferably in the range of 0.2/1 to 50/1 in a weight ratio. The particle size of the mixed catalysts of manganese dioxide and the above metal oxides is not limited specifically; however, fine powder such as 0.5 μm or less is not generally preferable because of excessive load for the filter in filtration step.

【0011】

In the present invention, the content of the specified mixed catalysts is not limited, but normally 1 through 40% by weight, preferably 3 through 30% by weight, and more preferably 3 through 15% by weight, of the total weight of the composition that includes the gas generant containing the nitrogen-containing organic compound and oxygen-containing inorganic oxidizer as the essential components and a blended third component. Too much specified mixture content is not desirable because the amount of generated gas is decreased against unit weight of the gas generant composition; and too little content is not desirable because the effect of decreasing toxic gas concentration is unsatisfactory.

【0012】

For the purpose of enhancing the shaped strength of the gas generant composition, a binder, a decomposition promoter of nitrogen-containing organic compound, silica or the like may be blended. Examples of the binder include: fine crystal binders such as marketed under the trade name "Avicel"; polymer binders such as poval; organic binders such as starch. As a decomposition promoter of nitrogen-containing organic compound, an inorganic decomposition promoter or an organic decomposition promoter can be used. Examples of an inorganic decomposition promoter are, specifically, ZnO, $ZnCO_3$, $FeCl_3$, Pb_3O_4, PbO_2, PbO, Sb_2O_3, TiO_2, V_2O_5, CeO_2, Ba_2O_3, CaO_2, YbO_3 and the like. An example of the organic decomposition promoter can be urea.

[0013]

The composition according to the present invention is prepared by blending respective components mentioned above; resulting blended composition may be used as such for a gas generant, however, a formulated form is preferable. Any known methods are applicable for the formulation, and a suitable binder may be selected. Shape of the formulated composition is not limited specifically and may be, for example, pellet, disc, ball, like-confetti, and like-tetrapod. The formulated composition may be without holes or with holes (such as briquette with holes or ring shape).

[0014]

【Effect of the Invention】

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, toxic components in the released gas, in particular nitrogen oxides, can be reduced to a practical level which is acceptable as an air bag system for automobile.

【0015】

【Examples】

Now, the present invention is explained more specifically concerning the first to fifth embodiments by way of examples; however, the present invention is not limited to these examples if not out of the scope and spirit of the invention.

Hereinafter, "parts" and "%" are based on weight unless otherwise specified.

【0016】

Example 1

Ten parts of manganese dioxide (manufactured by NAKARAI TESQUE, INC.), 10 parts of copper (II) oxide (N-300, manufactured by Nissin CHEMCO, Ltd.), 30 parts of azodicarbonamide, 35 parts of potassium perchlorate and 35 parts of strontium nitrate were mixed well; furthermore, 5% aqueous solution of a soluble starch was added therewith so that the starch content be 0.55 parts. Resulting humid

fine particles were adjusted to suitable fineness and water content for shape formulation, and formed into pellets (9.7 mmϕ x 4 mmϕ). The pellets were subjected to a predetermined tank test (as described in JP-B 52-3620 and JP-B 64-6156) using a burning device equipped with a filter and coolant; thereby, the concentration of nitrogen oxides in the gas generated in the tank was evaluated. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 600 ppm as determined by a gas detector tube.

[0017]

Example 2

Example 1 was repeated except that 10 parts of copper (II) oxide was replaced by 10 parts of tricobalt tetroxide (manufactured by NAKARAI TESQUE, INC.) to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 500 ppm.

[0018]

Example 3

Example 1 was repeated except that 10 parts of copper (II) oxide was replaced by 10 parts of iron (III) oxide (manufactured by NAKARAI TESQUE, INC.) to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were

of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 700 ppm.

[0019]

Example 4

Example 1 was repeated except that 10 parts of copper (II) oxide was replaced by 10 parts of silver (I) oxide (manufactured by NAKARAI TESQUE, INC.) to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 650 ppm.

[0020]

Example 5

Example 1 was repeated except that 10 parts of copper (II) oxide was replaced by 10 parts of copper (I) oxide (manufactured by NAKARAI TESQUE, INC.) to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 600 ppm.

[0021]

Comparative Example 1

Example 1 was repeated except that 10 parts of copper (II) oxide was not added to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were

of desired values. The concentration of nitrogen oxides in the gas generated in the tank was not less than 2,000 ppm.

[0022]

Comparative Example 2

Example 1 was repeated except that 10 parts of manganese dioxide was not added to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was not less than 2,000 ppm.

[0023]

Example 6

Example 1 was repeated except that 5 parts of silver (II) oxide was further added to the starting mixture to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 440 ppm.

[0024]

Example 7

Example 2 was repeated except that 5 parts of silver (II) oxide was further added to the starting mixture to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The

concentration of nitrogen oxides in the gas generated in the tank was 370 ppm.

【0025】

Example 8

Example 1 was repeated except that the amount of catalyst addition was changed to 25 parts of manganese dioxide and 2 parts of copper (II) oxide to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 630 ppm.

【0026】

Example 9

Example 1 was repeated except that the amount of catalyst addition was changed to 20 parts of manganese dioxide and 0.5 parts of copper (II) oxide to evaluate the concentration of nitrogen oxides in the gas generated in the tank. The burning pressure and period were of desired values. The concentration of nitrogen oxides in the gas generated in the tank was 1,240 ppm.

【Designation of Document】 Abstract

【Abstract】

【Object】 To provide a gas generant composition which decreases toxic components, in particular nitrogen oxides, in generated gas to a concentration practical as an air bag system for automobile.

【Structure】 In the gas generant composition, a nitrogen-containing organic compound such as a compound containing amino group or amido group or a tetrazole derivative and a oxygen-containing inorganic oxidizer such as KNO_3, $Sr(NO_3)_2$ or $KClO_4$ are essential components. And further, mixed catalysts comprising manganese dioxide and one or at least two metal oxides selected from the group consisting of copper oxides, cobalt oxides, iron oxides and silver oxides.

【Selected Drawing】 none

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[Corrected Document] Patent Application

(Recognized and added Information)

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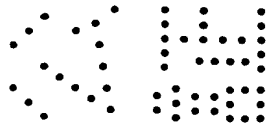

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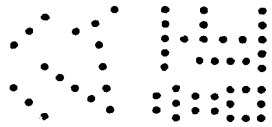

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